A Laboratory Quick Test for Predicting the Lime Requirement of Acid Mineral Soils

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Summary

In the summer of 1970, field and laboratory lime rate studies were started on seven acid soils from western Washington. The purpose was to determine the accuracy of the Shoemaker, McLean and Pratt (SMP) buffer procedure (15) for predicting the amount of lime required to obtain selected soil pH levels. The SMP procedure overestimated the lime requirements found by field testing but predicted lime requirements of the same order of magnitude as those found by laboratory incubation tests. This result was explained by the generation of a considerable amount of soil acidity during laboratory incubation of the soils.

Although lime requirement predictions by the SMP procedure are based solely on the pH of the soil-SMP buffer mixtures (pH_{SMP}), our studies indicate that lime requirements are also a function of the soil pH determined in .01 M CaCl₂ (pH_{Ca}). Equations using the independent variables, pH_{Ca} and pH_{SMP}, adequately predicted field lime requirements. Modifications were made in the original SMP procedure; both the SMP buffer and the method of measuring the pH_{SMP} were changed to improve the precision and simplicity of the measurement.

The accuracy of the proposed procedure was confirmed by tests begun in the winter of 1973 on 16 western Washington soils. Actual lime requirements were found by mixing increments of limestone with the soils that were packed in tubes and allowed to react under field conditions for 18 months. During this time, periodic pH_{Ca} determinations were made.

Introduction

The addition of basic materials to acid soils alters many soil parameters, making it hard to establish which changes are responsible for improved plant vigor. The one measureable parameter most reflective of all others is the soil pH. It seems sensible, therefore, to define lime requirement in terms of the quantity of basic material needed to produce a suitable soil pH. However, if soil pH is to be useful for comparisons, conditions of measurement must be specified and relatively constant.

When soil pH is determined in .01 M CaCl₂ (pH_{Ca}), many problems associated with measurement of the soil pH in water are alleviated (12, 14, 18). The soluble salt levels common to humid region soils have little effect on pH_{Ca} values. Moreover, such values are not affected by the soil-to-solution ratio until the ratio becomes very small. Liquid junction potentials can result in erroneous electrometric pH measurements. Clark (7) found that this source of error was eliminated when measurements were made in .01 M CaCl₂ solutions. Some laboratories determine pH in M KCl to blank out salt effects. However, the pH of soils suspended in salt solutions of this magnitude is strongly affected by the soil-to-solution ratio.

For western Washington soils, it has been found that most vegetable and field crops produce maximum growth between pH_{Ca} 5.3 and 5.4; response to lime generally is questionable or small for soils having pH_{Ca} levels between 5.1 and 5.3 (2, 3, 5). For a crop like alfalfa, which requires a high pH for establishment, the pH_{Ca} should be about 5.8 (4). These values correspond closely to the findings of Fisher (9) for a variety of crops in Missouri. Some important crops grown in western Washington (e.g., potatoes and strawberries) do not require a pH_{Ca} as high as 5.4 for maximum yields. However, they are often grown in rotation with other crops that do (2).

It is generally recognized that CaCO₃ reacts slowly with soils because of its low solubility. Moreover, some portions of soil acidity are only slowly neutralized. Thus, it is a common practice to recommend that lime be incorporated in late summer or early fall to obtain favorable pH levels by the following spring. However, it is not uncommon for a grower to apply lime in the spring in the hope of obtaining a partial benefit during the current season and full benefit the following year.

With the above in mind, "lime requirement" will be defined as the minimum amount of $CaCO_3$ equivalent required to bring the pH_{Ca} up to 5.4 or 5.8 within 6 months to a year after the liming material has been thoroughly mixed with a specific volume of soil. It was the purpose of this study to develop a laboratory procedure for predicting such lime requirement values.

Initial Studies

Experimental

During the summer of 1970, seven field sites were selected for study. The properties of the soils at these sites are described in table 1. Predicted lime requirements to obtain a water pH of 6.0 (using 5 g H₂O per 5 g soil) was determined by the buffer procedure of Shoemaker, McLean and Pratt (15), using their table for the application of pure CaCO₃. This procedure is used in many states, and is commonly called the SMP procedure.

As it was our desire to use pH_{Ca} as the basis for liming, it was necessary to convert distilled H_2O pH values to pH_{Ca} values. It was assumed that a soil with a pH of 6.0 will have a pH_{Ca} of approximately 5.4. We found that the difference between the pH in H_2O and pH_{Ca} averaged about 0.6 pH units, provided that the soil was immediately spread out to dry at room temperature and had not been recently fertilized.

Peech (13) states that this difference averages between 0.5 and 0.6 units. The difference will be very small or insignificant when soils are high in soluble salts. When soils are leached to remove traces of soluble salts and spread thinly to dry rapidly (in about 1 hour) in a forced

TABLE 1. Physical and chemical characteristics of soils used for the initial studies

				Organic	matter				
Series name	Textural class	Clay Si	lt Sand	H ₂ O ₂ oxidized	Walkley (18)	pH _{Ca}	pH _{SMP} 1	Exchange acidity CEC	BS
				*****				meq/100 g	1
Nisqually	Lo Sa	5.6 12	.1 82.3	3.6	5.6	4.57	6.07	1.12 7.5	4.8
Norma	Si Lo	14.6 61	.0 24.4	4.9	6.8	4.60	5.83	1.25 25.1	43.4
Puyallup	Sa Lo	5.9 28	.7 66.4	2.1	3.1	4.70	6.50	.67 9.2	61.4
Buckley	Lo	14.6 32	.7 52.7	8.8	12.1	4.80	5.49	.80 18.4	52.9
Alderwood	Lo	14.7 47	.4 37.9	6.1	8.3	4.90	5.95	.45 17.7	55.1
Kitsap	Lo	23.9 45	.4 30.7	5.1	7.4	5.10	6.05	.20 21.3	64.6
Sultan	Si Lo	9.4 75	.0 15.6	1.9	3.2	5.30	6.76	.02 12.8	79.3

¹pH of SMP buffer and soil mixture using a 20 minute reaction time.

draft at room temperature, the difference may be as great as 1.0 to 1.2 pH units.

Bulk soil samples were procured from each site to a depth of 8 inches. These were air dried, and the fraction that passed a 2-mm sieve was used for laboratory incubation and titration studies. The weight of gravel and stones (>2 mm) in each sample was determined, so that it was possible to calculate the amount of lime applied to the field per unit of <2-mm material. This made data from field and laboratory studies more strictly comparable.

Calcitic limestone flour¹ (having a minimum of 100% 10 mesh, 90% 60 mesh and 80% 100 mesh material; a minimum of 97% CaCO₃ and a maximum of 2% MgCO₃) was applied by hand spreading to 15- x 15-foot plots at each site. Rates used were 0, 0.5, 1.0, 1.5, 2.0 and 3.0 times the predicted amount of lime required to attain a pH_{Ca} of 5.4 by the SMP procedure. The treatments were randomized in four replications. The lime was incorporated to a depth of 8 inches by rotovating 4 times. Later, the plot area was seeded with orchard grass and ladino clover. Samples were procured periodically from the center of the plots for the determination of pH_{Ca} values.

Laboratory incubation tests were run, using 200 g of soil and rates of precipitated, reagent grade CaCO₃ of 0, 0.33, 0.67, 1.0, 1.5, 2.0 and 3.0 times the amount of lime required to attain a pH_{Ca} of 5.4 as predicted by the SMP method. The CaCO₃ and dry soil were thoroughly mixed, placed in plastic beakers, wet to field capacity, and covered with 1-mil polyethylene films secured with rubber bands. The soils were incubated at room temperature (20 to 25 C) and brought to field capacity periodically by adding distilled H₂O to produce a predetermined weight. Three sets of each treatment were established; one set was terminated after each of 6, 9 and 12 months of incubation.

During the same period, another set of incubation tests was set up that differed from the above only in the

method of mixing the CaCO₃ and soil. The mixing procedure was designed to simulate the type of mixing that usually occurs in field operations. The soil was spread on a sheet of plastic and the CaCO₃ streaked in 3 lines across the surface, covering about 15% of the surface. To make the soil and CaCO₃ coalesce, just enough water was added to moisten the lines, leaving the bulk of the soil dry. The soil was transferred to a plastic beaker and poured back and forth 4 times between 2 beakers before being moistened to field capacity and covered for a 12-month incubation.

After drying all soils from the incubation studies, they were crushed and thoroughly mixed before determining their pH_{Ca} values. Curves of pH_{Ca} vs. meq of added CaCO₃/100 g were constructed to estimate the lime required to attain the pH_{Ca} values of 5.4 and 5.8.

Soil samples procured from each site were titrated as follows: to flasks containing 10 g of soil and 50 ml of .01 M CaCl₂ were added 7 separate increments of standardized .195 M Ba(OH)₂ dissolved in .01 M CaCl₂. The flasks were sealed and the pH_{Ca} determined on the suspensions at intervals over a 7-day period. Titration curves were constructed to determine the amount of base required to attain the pH_{Ca} of 5.4 and 5.8.

To assay the effect of residual CaCO₃ on the pH_{Ca} measurements, CaCO₂ was added to soils at rates of .02% and .1% by weight. The pH_{Ca} was determined periodically during a 24-hour interval. The vessels were sealed between measurements to prevent evaporation. The following forms of CaCO₃ were used:

- 1. Precipitated, analytical grade CaCO₃.
- 2. Limestone flour used in the field plots. It was found by wet sieving that 62% of this material passed a 270-mesh screen).
- 3. The fraction of limestone flour remaining on a 270-mesh screen after wet sieving.

Particle size distribution of the soils was estimated by the pipette method (8) after destruction of organic matter with H₂O₂ and dispersion of the colloids in boiling

¹ This is the most common liming material used in western Washington.

Na₂CO₃. H₂O₂-oxidizable organic matter was determined gravimetrically during preparation of the soils for mechanical analysis and also by the Walkley procedure (17). Exchange acidity was determined by titrating a 1 M KCl extract of the soils with standardized Ba(OH)₂ after removing CO₂ from the extract by boiling.

Cation exchange capacity (CEC) was determined by saturating the soils with Ca using neutral, 0.5 M CaOAc and extraction of the exchangeable Ca with neutral, 1 M NH₄OAc. Exchangeable bases were also extracted with neutral, 1 M NH₄OAc. Ca and Mg were determined by atomic absorption and K and Na by flame emission on the NH₄OAc extracts. The procedure for determining pH_{Ca}

(soil pH in .01 M CaCl) will be given in the section headed "Proposed Procedure".

Field incubation and titration studies compared

There was little agreement among the 3 procedures for determining the lime required to attain the pH_{Ca} of 5.4 or 5.8 (table 2). The incubation procedure generally showed much higher lime requirements than those found by field tests. This is consistent with the fact that room temperature incubation resulted in marked depressions in the pH_{Ca} values of unlimed soils (table 3). Keogh and Maples (10) also noted a drop in pH values of soils stored

TABLE 2. Comparison of the predicted amount of $CaCO_3$ required to attain pH_{Ca} values of 5.4 and 5.8 as predicted by the Shoemaker et al., Procedure with those found by incubation, field tests and titration

Series name	pH _{Ca} sought	Good	Incuba mix tion t		Poor mix onths		ld test	ts -months		Titra		lays	Predicted by SMP buffer method
			9			 12	16	24 red - med	0	1	2	7	
Nisqually	5.4 5.8	4.4 6.7		4.7 6.7	3.4 4.7	2.6 5.2	3.2 5.3	3.0 8.0	1.4 2.5	2.0 3.4		2.4	5.3 6.3
Norma	5.4 5.8	7.0 10.2		7.6 11.2	5.7 7.3	4.7 10.0	5.3 10.7	5.6 11.2	1.1 2.6	2.2 3.7	2.6	3.8 6.0	7.0 8.3
Puyallup	5.4 5.8	3.0 4.2		3.4 5.0	2.6 3.4	1.8	1.5 4.1	1.5 4.2	0.6 1.0	0.8		0.9	2.7 3.3
Buckley	5.4 5.8	9.0 15.5		10.4 17.4	7.7 10.0	3.6 8.0	4.0 8.0	2.8		2.6 4.8		3.2 6.0	9.1 10.9
Alderwood	5.4 5.8	6.0 10.4	6.5 10.4	6.9 11.9	4.3 7.3	1.2	1.8 6.8	1.5 8.8	0.5	0.6		1.3 3.1	6.2 7.4
Kitsap	5.4 5.8		3.5 7.1		3.5 5.4	0.0 3.3	0.2	0.4 4.4	0.2			0.7 2.2	5. 6 6.7
Sultan	5.4 5.8	0.5 1.5		0.5 1.7	0.6 1.4	0.0	0.0	0.0 3.5	0.0	0.0		0.0	1.1 1.4

TABLE 3. Change with time in pH_{Ca} values of unlimed incubated and field plot samples

Series name		Incubated samples Reaction time-months				1d sampl on time-	amples ime-months	
•	0	6	9	12	12	16	24	
Nisqually	4.57	4.32	4.26	4.30	4.55	4.49	4.80	
Norma	4.60	4.40	4.35	4.33	4.73	4.67	4.70	
Puyallup	4.70	4.47	4.42	4.47	4.86	5.02	5.10	
Buckley	4.80	4.70	4.61	4.60	4.86	4.94	4.90	
Alderwood	4.90	4.80	4.75	4.66	5.06	5.17	5.20	
Kitsap	5.10	5.03	4.95	4.97	5.45	5.37	5.36	
Sultan	5.30	5.20	5.21	5.11	5.47	5.50	5.43	

in a moist state for 32 days and recommended that soils be dried soon after sampling. We can only speculate on the reason for the development of more acidity with room temperature incubation than under field conditions. Undoubtedly, conditions for microbiological activity are enhanced with the higher temperature and continuous optimum moisture under incubation, resulting in more mineralization of acidifying anions such as NO₃, SO₄ and PO₄. Under field conditions, a large portion of such anions are removed by growing plants and replaced by HCO₃ which is eliminated, in large part, by the diffusion of CO₂ to the atmosphere under well drained conditions.

Lime requirements predicted by the SMP procedure are generally about the same as those found by incubation (table 2). This is not surprising, for lime requirements predicted by this procedure were calibrated using incubation tests. It is clear, however, that calibration in this manner results in an overestimation of lime required under field conditions.

On the other hand, titration generally underestimated the amount of lime required for the field, even when equilibrated for as long as a week, (table 2). Apparently, a significant fraction of the acidity in these soils is only slowly neutralized. These results conflict with the findings of Shoemaker et al. (15); they reported that their buffer procedure resulted in lime requirement values that were similar to that found by a Ca(OH)₂ titration procedure (which was not described).

Despite the lack of exact agreement, titration generally provides lime requirement values that correlate well with actual field values. Thus, it is possible to derive a best-fit equation to correct titration values to actual field lime requirements. Because titration requires considerable time and laboratory expertise, we thought that modification of the buffer procedure would be more practical.

Close scrutiny of the data indicated that actual lime requirements were a function of the initial pH_{Ca} as well as the pH of the SMP buffer-soil mixture. For example, the pH of the buffer-soil mixture was about the same for the Kitsap and Nisqually soils (table 1), but the pH_{Ca} of the Kitsap was higher than that of the Nisqually soil. The amount of lime required to attain a pH_{Ca} of 5.4 or 5.8 in the field plots (table 2) was considerably greater for the Nisqually soil.

As a consequence of this, equations were empirically devised, using both variables to predict field lime requirements. These are given in the "Proposed Procedure" section. Adams and Evans (1) also found it necessary to use soil pH as well as buffer solution pH depression to predict field lime requirement values accurately.

Good and poor mixing of soil and CaCO₃ compared

It was observed (table 2) that less lime was required to bring the incubated soils to a pH_{Ca} of 5.4 or 5.8 when soils and CaCO₃ were not thoroughly mixed than when they were well mixed. The poorly mixed treatments contained significant amounts of residual CaCO₃ at all but the lowest lime rates. The presence of free CaCO₃, despite its low solubility, can increase the soil pH substantially,

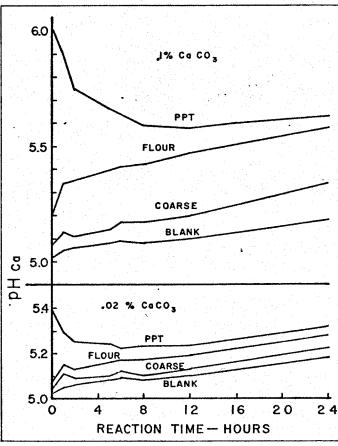
even in the relatively short time required for the measurement (with the pH normally being determined between 30 and 60 minutes after wetting).

Figure 1 illustrates the effect on pH_{Ca} of the addition of CaCO₃ of various size fractions to an acid soil. It is obvious that unreacted CaCO₃ can cause a marked increase in pH_{Ca} measurements. The amplitude of the increase depends on the quantity of added CaCO₃, its surface area, and the time between wetting and pH measurement.

The fact that very fine, precipitated CaCO₃ had been used for the incubation tests, and that pH_{Ca} measurements were made at a time (1 hour after wetting) when precipitated CaCO₃ was still close to its peak effect on pH_{Ca} (figure 1) explains the magnitude of the effect for the poorly mixed samples. These results may also explain why crop responses to a lime application are often noticeable even when it is incorporated just before planting (3).

The SMP buffer

The buffer devised by Shoemaker et al. (15) has several desirable properties for assaying the acidity of soils. It is dilute enough to be very sensitive. On titration, only .140 to .146 meq of HCl are needed to lower the pH of 10 ml of SMP buffer 1 pH unit over the pH range of 7.5



1. The effect of the amount and particle size of unreacted $CaCO_3$ on the pH_{Ca} of the Kitsap soil measured over a 24-hour period. The initial pH_{Ca} measurement was determined 5 minutes after wetting. Blank = no $CaCO_3$ added, coarse = the fraction of limestone flour coarser than 270 mesh, flour = the calcitic limestone flour used in the field tests, ppt = precipitated, reagent grade $CaCO_3$.

to 4.0. Moreover, the titration curve is remarkably linear over this range. The high concentration of CaCl₂ probably increases the exchange of acidic cations adsorbed on soil colloids.

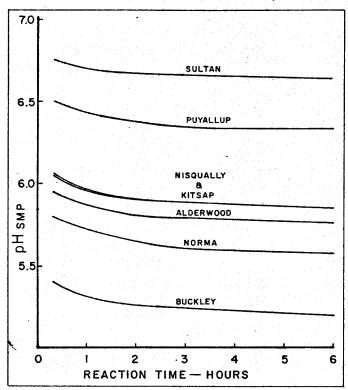
We found it desirable to modify some parts of the Shoemaker et al. (15) procedure. They specify that a specific volume of triethanolamine (TEA) be added to the buffer mixture and that the pH then be adjusted with NaOH. Because concentrated TEA is so viscous, we found it desirable to add a specific weight of TEA and adjust the pH with dilute TEA.

In the SMP procedure, 5 g of soil is moistened with 5 ml of H_2O prior to determining the pH in water and then 10 ml of SMP buffer is added and the pH of this final mixture is determined. As we do not determine the pH in water before determining the pH of the SMP buffersoil mixture, it is more convenient to add 15 ml of an SMP buffer that is 67% as concentrated as the original buffer.

We found that this change did not affect the pH of the SMP buffer-soil mixtures. The pH of the buffer changed from 7.5 to 7.6 on dilution of 10 ml of the original buffer with 5 ml of H_2O . Thus we adjust the pH of the more dilute SMP buffer to 7.6

Figure 2 shows that the pH of SMP-buffer-soil mixtures drops rapidly upon addition of the buffer, but that the change is very slow after 4 hours. We recommend that the pH routinely be determined 4 hours after the buffer addition in order to reduce errors caused by non-uniform timing during mass testing.

Some workers (6, 11) recommend varying the soilto-buffer ratio and multiplying the lime requirement by a factor related to the ratio change when the pH of soilbuffer mixtures is at either extreme of the lime requirement table. The data in table 4 show that this can result



2. The effect of reaction time on the PH of SMP buffer-soil mix tures. The initial measurement was made 20 minutes after the buffer addition.

in large errors, because the smaller the soil-to-buffer ratio, the greater the proportion of soil acidity neutralized. This error probably results from the neutralization of more pH-dependent soil acidity when the ratio is low, because the final pH of the soil-buffer mixture is higher at the low ratio.

TABLE 4. The effect of the soil-to-SNP buffer ratio on the pH of the mixture and on the amount of H ion neutralized by the buffer

	g soi	1/10 ml	buffer	g soi	l/10 m1	buffer
Series name	2.5	5.0	10.0	2.5	5.0	10.0
	рН	of mixt	ure ¹	meq. I	I/100 g	soil ²
Nisqually	6.33	5.89	5.47	6.69	4.60	2.90
Norma	6.11	5.59	5.07	7.95	5.46	3.47
Puyallup	6.74	6.34	5.87	4.35	3.32	2.33
Buckley	5.70	5.24	4.90	10.30	6.46	3.72
Alderwood	6.21	5.79	5.39	7.38	4.89	3.02
Kitsap	6.28	5.87	5.46	6.98	4.66	2.92
Sultan	6.95	6.65	6.23	3.15	2.43	1.82

¹After a 4-hour reaction time.

²Calculated from the average amount of H ion required to depress the buffer pH one unit (.143 meq H/pH unit).

It is also obvious from this that the greater the neutralizable acidity per unit weight of soil, the smaller the proportion of this acidity that will be neutralized by the buffer at a constant soil-to-buffer ratio. This may, at least, partially explain the necessity of increasing the predicted lime requirement as the initial pH_{Ca} decreased.

Proposed Procedure

Reagents '

3.6 M CaCl₂. Dissolve 529.3 g of CaCl₂·2H₂O in distilled H₂O and bring the volume to 1 liter.

.01 M CaCl₂. Transfer 50 ml of 3.6 M CaCl₂ to a carboy and dilute to 18 liters with distilled H_2O . Adust the conductivity of this solution to $2.32 \pm .08$ mmho/cm at 25 C with distilled H_2O or with 3.6 M CaCl₂.

Modified SMP buffer. Place 1.2 g of paranitrophenol in a 1-liter volumetric flask and dissolve in about 800 ml of distilled H₂O. Dissolution occurs in about 16 hours (overnight) or considerably faster with continuous shaking. Add 1.87 g of triethanolamine and then dissolve 2.0 g of K₂CrO₇, 1.33 g of Ca(OAc)₂·H₂O and 35.4 g of CaCl₂·2H₂O in the solution. Bring the volume to about 975 ml and adjust the pH to 7.6 with dilute (1:10) triethanolamine and bring the volume to 1 liter with distilled H₂O.

Procedure

Transfer a level teaspoon of air-dry, sieved (2mm) soil to a 50-ml beaker and add 25 ml of .01 M CaCl₂. Stir with a glass rod 3 times in about 30 minutes, allow to stand for 30 more minutes, and stir just before inserting the electrodes. When the meter needle ceases to drift, remove the beaker, stir again, reinsert the electrodes and record the pH_{Ca} reading immediately.

If the pH_{Ca} is 5.4 or higher, no lime is required for vegetable crops, grain, or forage crops (except alfalfa or sweet clover). If alfalfa or sweet clover are to be established, no lime is required if the pH_{Ca} is 5.8 or higher.

If the pH_{Ca} is below the desired level, then determine the pH of the soil-buffer mixture (pH_{SMP}) as follows: Transfer 5 g of air dry, sieved soil to a 25 ml Erlenmeyer flask, add 15 ml of SMP buffer, and stopper the flask. Swirl the contents 3 times in about 20 minutes. After a reaction time of 4 hours, swirl the contents and insert the electrodes half way into the suspension². When the meter needle ceases to drift, remove the electrodes, swirl the container, reinsert the electrodes, and record the pH_{SMP} reading immediately.

When the pH_{Ca} is below 5.4, use the following equations to predict the lime requirement:

- [1] $L_{5.4} = 2 (6.80 pH_{SMP}) (6.00 pH_{Ca})$
- [2] $L_{5.8} = L_{5.4} \cdot F$

When the pH_{Ca} is between 5.4 and 5.8, then

[3] $L_{5.8} = 2 (7.2 - pH_{SMP} - 4 (pH_{Ca} - 5.4))$ where $L_{5.4}$ and $L_{5.8}$ are the amounts of lime required in tons/acre 8 inches to obtain a pH_{Ca} of 5.4 and 5.8, re-

TABLE 5. The factor "F" required to convert $L_{5.4}$ values to $L_{5.8}$ values, based on pH_{Ca}

pH _{Ca} range	F -	
<4.70	1.60	
4.70-4.85	1.75	
4.86-5.00	1.85	
5.01-5.10	2.0	
5.11-5.20	2.5	
5.21-5.30	3.0	
5.31-5.39	3.5	

spectively. The factor F varies with pH_{Ca} as shown in table 5.

If it is known that the depth of mixing will vary from 8 inches the lime requirement can be adjusted by multiplying $L_{5,4}$ or $L_{5,8}$ by the intended incorporation depth in inches and dividing by 8.

The calculated lime requirement is based on the use of flour limestone, as described in the "Experimental" section. If the neutralizing power of the liming material to be used differs appreciably from 100%, adjust the lime requirement by multiplying L_{5.4} or L_{5.8} by the reciprocal of the CaCO₃ equivalent. If the limestone to be used is coarser than the limestone flour used in this study, adjust the lime requirement by using the Iowa method (16) for calculating the percent of limestone available as a function of fineness.

When the soil has considerable mineral material larger than 2 mm, $L_{5.4}$ or $L_{5.8}$ can be adjusted by multiplying by a factor (N) computed according to the equation:

$$N = \frac{A/1.4}{A/1.4 + B/2.6} = \frac{.71A}{.71A + .38B}$$

where A is the % by weight of dry soil that is finer than 2 mm and B is the % by weight of dry material that is coarser than 2 mm. This calculation is based on the assumption that the bulk density of the fine material is 1.4 and that the specific gravity of the coarse material averages 2.6. It is assumed that the spaces between the coarse material are filled completely with the finer fraction. Even if the bulk density of the fines deviates from 1.4, it does not result in a large error because this value (A/1.4) occurs in both the numerator and the denominator.

From the practical standpoint, we recommend that calculated lime requirements below .5 tons/acre be rounded to .5 tons/acre. It is also expedient to round all recommendations to multiples of .5 tons/acre. For calculated lime requirements deviating by .1 ton or less from the nearest .5-ton rate, round to the nearest multiple. For those with deviations greater than .1 tons/acre, round to

² We use a micro-electrode pair; but if larger electrodes are to be used, a wide-mouthed vessel will be needed, and the amount of soil and buffer should be doubled.

the next highest multiple. For example, if $L_{5.4}=3.10$, recommend 3.0 tons/acre. If $L_{5.4}=3.15$, then recommend 3.5 tons/acre.

Test of the Proposed Procedure

Experimental

Bulk samples consisting of the 0-8 and 8-16 inch layers of 16 soils from western Washington were collected, sieved through a 1/4-inch streen and air dried. Before we dried the bulk samples, subsamples were taken and dried rapidly to prevent any extended incubation. These samples were sieved through a 2-mm screen and used to determine pH_{Ca}, pH_{SMP} by the SMP (15) and the proposed procedures, and other variables listed in table 6. Table 7 provides classification data for these soils.

To simulate field conditions, all soils were packed into cylinders that had been buried in a well-drained area of Sultan silt loam. They were buried so that the top edge of the cylinders extended about 1/4-inch above the surrounding soil surface. The cylinders were 16 inches long and had an 8 inch inside diameter. They were made of 1/2-inch thick, wax impregnated cardboard and are ordinarily used as forms for concrete column construction.

Subsoil from each soil series was packed into the bottom 8 inches of each of 9 cylinders. Surface soil of the same series then was thoroughly mixed with limestone flour at rates of 0, .5, 1, 1.5, 2 and 2.5 times the L_{5.4} predicted by the proposed procedure, and each mixture was packed into the upper 8 inches of one of the cylinders. In addition, "poor" mixtures of limestone flour and soil were made of rates of .5, 1 and 2 times the L_{5.4} predictions. The latter were designed to simulate the type of mixing that occurs during ordinary field operations, and were mixed in roughly the same manner as described for the laboratory incubation tests. The cylinders were covered to maintain all in a dry state until the entire operation was completed.

On February 26, 1973 all covers were removed, and bentgrass broadcast over the surface, followed by careful watering to wet at least the surface 8 inches of soil. Surface soil samples were procured from the thoroughly mixed soil-lime treatments 4, 6, 10, 16 and 18 months after the initial watering. The "poorly" mixed treatments were sampled only on the 10-and-18 month sampling dates. In all but the last sampling date, 2 cores were removed from the top 7 inches, the 1-to 7-inch layer from each core was thoroughly mixed, and a level teaspoonful was removed from the pH_{Ca} determination. The remaining soil was then returned to the core holes.

On the last sampling date, four 1-to 7-inch cores were removed from each cylinder and the entire sample air dried, sieved through a 2-mm sieve, and subsampled for the determination of pH_{Ca}. The pH_{Ca} values were used to construct titration curves from which actual lime requirements were ascertained for each soil on each sampling date.

The pH_{SMP} values were determined both by the proposed method and by that of Shoemaker et al. (15) on those samples that had pH_{Ca} values between 5.4 and 5.8

on the last sampling date. This was done to enable us to devise a best fit equation for predicting $L_{5.8}$ values for soils in this pH_{Ca} range, as this had not been done before.

When estimating lime requirements from the original Shoemaker et al. (15) procedure, we had to make several assumptions. We used their table relating pH_{SMP} to the lime requirement when pure CaCO3 is to be used. This table had been calibrated against incubation tests on which lime requirement was calculated as tons of CaCO₃/2,000,-000 lb of soil. For soils averaging 1.47 bulk density, this could be interpreted as the lime requirement/acre 6 inches of soil. The soils in our test had a mean bulk density of 1.32, so that there would be 2,000,000 lb of soil in an acre 6.68 inches. As we mixed our lime to a depth of 8 inches, we multiplied their table values by 1.2 (i.e., 8 ÷ 6.68) to obtain predicted lime requirement by the original SMP procedure. Obviously, higher values would have been predicted by the SMP method had we based our calculations on a 6-inch depth of incorporation or had we used their published (15) table for the use of agricultural limestone.

Results and discussion

Regression analyses indicated that the proposed procedure for predicting the quantity of limestone flour required to bring the pH_{Ca} to 5.4 or 5.8 gave better agreement with field lime requirement values than did the method of Shoemaker et al. (15). See figures 3 & 4, tables 8 & 9. As was noted in the initial studies, the original SMP procedure overestimates actual field lime requirement values. A fair estimate of actual lime requirements can be obtained simply by reducing their predicted lime requirements by about 2 tons/acre for L_{5.4} and 1 ton/acre for L_{5.8}. However, the proposed procedure resulted in higher correlation coefficients (tables 8 and 9) especially for L_{5,4} predictions; thus the accuracy of the predictions was improved by considering pH_{Ca} as well as pH_{SMP}. Figure 5 shows how the original SMP procedure grossly overestimates L_{5,8} when the pH_{Ca} of soils are in the range of 5.4

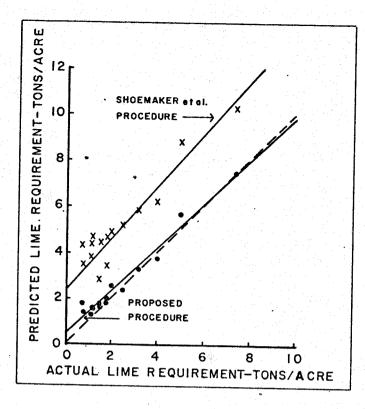
When lime is incorporated under field conditions, it is not practical to obtain a homogeneous mixture, even with rotovating equipment. To evaluate this, the effect on pH_{Ca} of simulated, practical lime incorporation (poor mixing) was compared with thorough mixing at three rates of lime.

Table 10 shows that pH_{Ca} values were generally close for both mixing procedures. At the higher rates of lime, mean pH_{Ca} levels were slightly lower with poor mixing. Figures 3, 4 and 5 show that the proposed procedure predicts slightly more than the actual amount required with thorough mixing. In addition, the proposed rounding procedure, which was not used in these tests, favors slightly higher lime recommendations. These should compensate for slightly lower pH_{Ca} values obtained with incomplete mixing of lime with the soil.

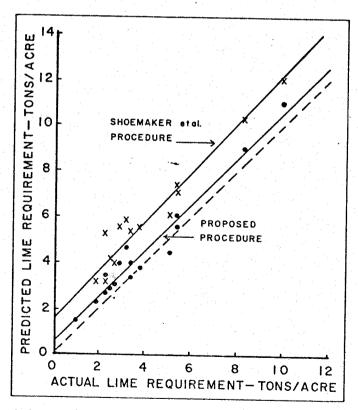
The pH_{Ca} was measured at both 5 minutes and 1 hour after wetting on the "poorly" mixed samples procured after the 10-month reaction time. The pH_{Ca} values did not change appreciably during this time period, indicating that

Series name	Textural class	pił _{Ca}	pH _{SMP}	Clay	Silt	Sand	Organic H ₂ O ₂ oxidized	Walkle
Puyallup	Sa Lo	4.83	6.23	4.9	38.1	57.0	2.3	2.9
Sultan	Si Lo	4.95	6.22	11.8	58.7	29.5	2.6	3.1
Puget	Si Cl Lo	5.08	5.87	32.4	66.3	1.3	5.8	9.8
Newburg	Lo	4.99	5.84	12.2	38.9	48.9	4.1	6.0
Newburg	Si Lo	4.54	5.50	23.8	58.3	17.9	4.1	5.8
Chehalis	Si Lo	4.75	5.76	21.4	62.9	15.7	3.4	4.9
Mapato	Si Cl Lo	4.34	4.68	32.2	64.2	3.7	9.8	14.3
Salkum	Si Lo	4.98	5.78	14.2	52.1	33.7	2.9	4.0
Lauren	Sa Lo	5.17	6.55	7.6	17.5	74.9	1.1	1.7
Felida	Lo.	4.73	6.08	12.3	49.5	38.2	1.6	2.4
Alderwood	Lo	4.89	5.72	11.2	43.5	45.3	4.6	6.8
Norma .	Si Lo	5.20	5.80	13.8	69.0	17.2	5.4	8.9
Buckley	Lo	4.43	4.98	11.3	38.8	49.9	9.1	13.0
Kitsap	Lo	5.05	6.06	14.4	42.2	43.4	3.7	5.7
Visqually	Lo Sa	4.60	5.57	4.4	17.4	78.2	5.8	9.1
Olympic	Si Lo	5.16	5.85	15.8	68.9	15.3	4.8	8.2

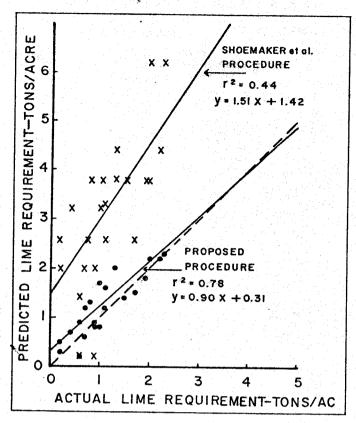
Series	Subgroup	Family
Puyallup	Fluventic Haploxerolls	coarse loamy over sandy or sandy skeletal, mixed, mesic
Sultan	Typic Udifluvents	fine silty, mixed, non-acid, mesic
Puget	Typic Fluvaquents	fine silty, mixed, non-acid, mesic
Newberg	Fluventic Haploxerolls	coarse loamy, mixed, mesic
Chehalis	Cumulic Ultic Haploxerolls	fine silty, mixed, mesic
Wapato	Fluvaquentic Haplaquolls	fine silty, mixed, mesic
Salkum	Ultic Haploxeralfs	fine, mixed, mesic
Lauren	Cumulic Haploxerolls	loamy skeletal, mixed, mesic
Felida	Ultic Argixerolls	fine silty, mixed, mesic
Alderwood	Dystric Entic Durochrepts	loamy skeletal, mixed, mesic
Nonna	Fluvaquentic Immaquepts	coarse loamy, mixed, non-acid, mesic
Buckley	Typic Humaquepts	fine loamy, mixed, non-acid, mesic
Kitsap	Dystric Xerochrepts	fine loamy, mixed, mesic
Nisqually	Pachic Xerumbrepts	sandy, mixed, mesic
Olympic	Xeric Haplohumults	clayey, mixed, mesic



3. Comparison of laboratory procedures for predicting lime requirements to attain a pH_{Ca} of 5.4 with actual lime requirements found after 10 months of reaction time. The interrupted line is the ideal curve (y = x).



4. Comparison of laboratory procedures for predicting lime requirements to attain a pH_{Cn} of 5.8 with actual lime requirements found by liming soils after 10 months of reaction time. The interrupted line is the ideal curve (y = x).



5. Comparison of laboratory procedures for predicting lime requirements to attain a pH_{Ca} of 5.8 with actual lime requirements found by liming soils after 18 months of reaction time. Only those soil samples with pH_{Ca} values between 5.4 and 5.8 were used. The interrupted line is the ideal curve (y = x).

the finer fractions of the limestone flour had reacted with the soil. However, it is likely that less of the coarser fractions of the limestone had reacted with the soil on the poorly-mixed treatments than on the well mixed ones.

Conclusions

The use of room temperature incubation of incremental mixtures of CaCO₃ and soil to determine lime requirements overestimates the actual lime requirements determined by field testing. This occurs because soil acidity increases under room temperature incubation. On the other hand, rapid titration with a soluble base underestimates the field lime requirement found in field tests, because a significant portion of the soil acidity is only slowly neutralized.

The proportion of the acidity in a soil that is neutralized by the relatively weak SMP buffer solution is inversely proportional to the total acidity present. This is probably the reason that the accuracy of L_{5.4} predictions could be improved by increasing the lime requirement as the pH_{Ca} of the soil decreased.

The $L_{5.8}$ prediction is based on the $L_{5.4}$ and a factor. The factor, F, is influenced by the buffering capacity of the soil which in turn, is based on the pH_{Ca} . If, for example, two soils have the same $L_{5.4}$ but one has a pH_{Ca} of 5.0 and the other has a pH_{Ca} of 4.5, it is obvious that the former is more strongly buffered. Thus, for the for-

TABLE 8. Linear regressions between laboratory procedures (y) for estimating L_{5.4} and actual lime requirements (x) Reaction time-months Procedure Regression equation y = .89x + .55y = 1.05x + 2.46Proposed Shoemaker et al. Proposed .89x + .58y = 1.06x + 2.46Shoemaker et al. 10 Proposed' 97 y = .94x + .48 y = 1.11x + 2.36Shoemaker et al. .88 y = .88x + .38 y = 1.06x + 2.2216 . Proposed Shoemaker et al. .89 y = .94x + .21 y = 1.13x + 1.99Proposed Shoemaker et al.

mer, the $L_{5.4}$ should be multiplied by a larger factor to raise the pH_{Ca} another .4 units to pH_{Ca} 5.8.

Finally, it was concluded that the pH_{Ca} levels will generally be similar whether the lime and soil are mixed by a simulated field mixing technique or thoroughly mixed under artificial conditions, provided only that enough time has elapsed for most of the lime to react with the soil.

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TABLE 9. Linear regressions between laboratory procedures (y) for estimating $L_{5..8}$ and actual lime requirements (x)

Reaction time-months	Procedure	r²	Regression equation
4	Proposed Shoemaker et al.	.94 .91	y = .92x + .57 y = .97x + 1.61
6	Proposed	.91	y = 1.00x + .54
		.86	y = 1.04x + 1.60
10	Proposed	.96	y = 1.01x + .49
	Shoemaker et al.	.93	y = 1.06x + 1.51
16	Proposed	.96	y = .90x + .38
	Shoemaker et al.	.94	y = .95x + 1.39
18	Proposed	.94	y = .90x + .48 y = .94x + 1.51
	Shoemaker et al.	.91	y = .94x + 1.51

TABLE 10. The effect of thorough (good) and incomplete (poor) mixing of lime with soil on the pH_{Ca} after 18 months of reaction time

Proportion of	predicted	L _{s 4}	applied

	•	.5	1		2		
	mixi meth			ing hod	mixing method		
	good	poor	good	poor	good	poor	
			pH _{Ca} v	alues			
Puyallup	5.06	5.15	5.45	5:41	6.12	5.87	
Sultan	5.22	5.19	5.52	5.58	6.10	5.96	
Puget	5.37	5.30	5.53	5.42	5.91	5.93	
Newberg Lo	5.25	5.16	5.44	5.40	5.78	5.78	
Newberg Si Lo	4.92	4.94	5.33	5.31	5.96	6.12	
Chehalis	5.16	5.07	5.51	5.41	6.02	6.08	
Wapato	4.79	4.80	5.22	5.18	5.90	5.70	
Salkum	5.13	5.11	5.29	5.30	5.70	5.50	
Lauren	5.29	5.34	5.50	5.55	5.70	5.68	
Felida	5.00	5.08	5.55	5.33	6.03	5.94	
Alderwood	5.11	5.06	5.34	5.33	5.78	5.78	
Norma	5.35	5.32	5.51	5.47	5.90	5.82	
Buckley	4.87	4.79	5.20	5.17	5.83	5.44	
Kitsap	5.20	5.17	5.48	5.29	5.78	5.74	
Nisqually	5.07	5.04	5.45	5.40	6.04	5.93	
Olympic	5.23	5.19	5.33	5.30	5.47	5.48	
Mean	5.13	5.11	5.43	5.37	5.88	5.80	
Mean							
(10 months)1	5.19	5.18	5.49	5.42	6.00	5.93	

The means of samples procured after 10 months of reaction time.

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Work was done under project 1999.

Published by the College of Agriculture Research Center, Washington State University, Pullman

May, 1977